

608. *The Halogen Cations in Aqueous Solution.*

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Thermodynamic and other physicochemical data on iodine, bromine, and chlorine have been used in the calculation of several new thermodynamic quantities. These include the free energies of formation in aqueous solution of the halogen cations  $X^+$  and  $H_2OX^+$  ( $X = I, Br, Cl$ ).

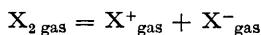
Electrometric measurements have been made on aqueous solutions of iodine in the presence of varying concentrations of silver salts and acid. It has been shown that, under certain experimental conditions, solutions containing considerable concentrations of an iodine cation can be prepared. The free energy of ionisation of iodine at  $25^\circ$  is found to be 15 kcal./mole, in good agreement with the free energy calculated for the reaction  $I_2 + H_2O = H_2OI^+ + I^-$ .

ALTHOUGH the cations of the halogens are now frequently invoked as agents in halogenation reactions, little evidence has so far been produced for their existence in measurable concentration in aqueous solution (Hinshelwood, *J.*, 1947, 694; De La Mare, Hughes, and Vernon, *Research*, 1950, 3, 192; Derbyshire and Waters, *J.*, 1950, 564; Sidgwick, "The Chemical Elements and their Compounds," Oxford Univ. Press, 1950, Vol. II, p. 1240). In this paper theoretical and experimental studies on the halogen cations are presented.

*Section A. Theoretical Considerations.*

An attempt has been made in this section to calculate the thermodynamic tendency for various halogen cations to be formed in aqueous solution. Throughout this paper, the symbol  $X$  stands for I, Br, and Cl; all thermodynamic data refer to  $25^\circ$  unless otherwise stated.

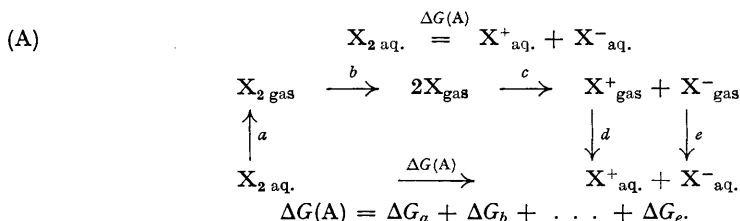
In the gas phase the tendency for halogen molecules to ionise with the formation of  $X^+$  is extremely small. The Gibbs free energy  $\Delta G$  of the reaction



is 195, 231, and 263 kcal./mole for iodine, bromine, and chlorine. These values are obtained from the known free energies of dissociation, ionisation potentials, and electron affinities (National Bureau of Standards, Washington, D.C.).

The tendency to ionisation increases enormously in aqueous solution because of the large heats of solution of the ions. The heats and free energies of solution of ions are obtained by one of the following methods. The free energies of solution of many salts have been obtained directly by experiment. The data for pairs of ions thus obtained can be analysed for single ions if a value for any one ion is assumed. The entropies of solution of ions are referred to the entropy of solution of the proton. The heats of solution of ions of equal charge and size are usually taken as equal. For example, the experimental values for potassium fluoride (radii of  $K^+$  and  $F^-$  are equal) provide a key for the heats of solution of many other single ions. It has, however, been shown theoretically that a negative univalent ion has a heat of solution about 2% higher than a positive ion of equal radius (Bernal and Fowler, *J. Chem. Physics*, 1933, 1, 515). The heats and entropies of solution of ions, obtained by this sort of analysis of experimental data, are in good agreement with the results of the *a priori* calculations by Eley and Evans (*Trans. Faraday Soc.*, 1938, 34, 1093). The free energies of solution of the ions  $X^-$  are taken from this paper. It will be seen later that the free energies of solution of  $X^+$  and  $H_2OX^+$  can be estimated in a similar manner.

We can now consider the tendency for the ionisation process (A) to occur in aqueous solution.



The free energies for steps  $a$ ,  $b$ , and  $c$  are well known. The free energies of solution of the ions in steps  $d$  and  $e$  are obtained by the method described above. The radii of the ions  $X^+$  can

be estimated from Pauling's data ("Nature of the Chemical Bond," Cornell, 1944) as 1.13, 0.96, and 0.84 Å for iodine, bromine, and chlorine. If the ions are spherical, their free energies of solution are estimated as -98, -111, and -120 kcal. It is almost certain that in aqueous solution the incomplete electron shell of these ions will be completed by a water molecule, giving ions of the type  $\text{H}_2\text{OX}^+$ . It is, however, of interest to consider what the ionising tendency would be if the cations were the bare ions  $\text{X}^+$  and were solvated by coulombic forces only.

We then have  $\Delta G(\text{A}) = \Delta G_a + \Delta G_b + \dots + \Delta G_e$ .

For iodine,  $\Delta G(\text{A}) = 0.7 + 28.9 + (242.2 - 75.7) - 98 - 43 = 55$  kcal.

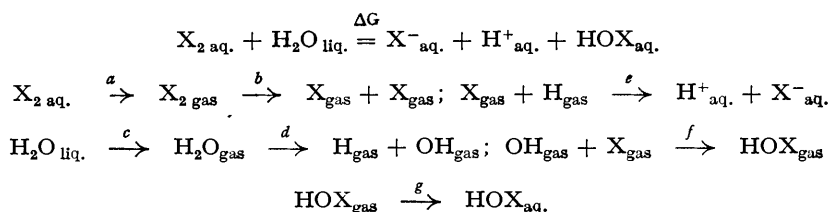
For bromine,  $\Delta G(\text{A}) = -0.2 + 38.6 + (274.6 - 82.1) - 111 - 53 = 67$  kcal.

For chlorine,  $\Delta G(\text{A}) = -1.0 + 50.4 + (300.3 - 87.3) - 120 - 58 = 84$  kcal.

These values correspond to equilibrium constants  $[\text{X}^-][\text{X}^+]/[\text{X}_2]$  of  $10^{-40}$ ,  $10^{-50}$ , and  $10^{-60}$ . The values for the free energies of solution of the positive ions  $\text{X}^+$  are of course approximate, but there can be no doubt that these bare cations cannot exist in appreciable concentration in aqueous solution.

A considerable stabilisation of the cations occurs when the covalent bond to a water molecule is formed and ions of the type  $\text{H}_2\text{OX}^+$  are produced. It will be seen later that the free energies of solution of the cations  $\text{H}_2\text{OX}^+$  and  $\text{X}^+$  are nearly equal, so that the stabilisation that occurs is mainly due to the free energy of formation of the oxygen-halogen bond.

*Free Energies of Formation of Oxygen-Halogen Bonds.*—The free energies of formation of the oxygen-halogen bonds in the compounds  $\text{HOX}$  (gas) can be calculated from the following thermodynamic cycle :



The free energy  $\Delta G$  of the hydrolysis reaction is the sum of the free energy changes  $a-g$ . The data used for this cycle are taken mainly from the tables of the National Bureau of Standards. The free energies of hydrolysis of the halogens have been measured by several workers (Bray and Conolly, *J. Amer. Chem. Soc.*, 1911, **33**, 1485; Liebhafsky, *ibid.*, 1934, **56**, 1500; Jakowkin, *Z. physikal. Chem.*, 1899, **29**, 613).

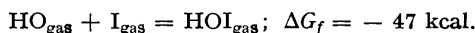
For iodine,  $\Delta G = 17.0 = 0.7 + 28.9 + 2.0 + 112.2 - 77.7 + \Delta G_f + \Delta G_g$   
 $\Delta G_f + \Delta G_g = -49.1$  kcal.

For bromine,  $\Delta G = 11.2 = -0.2 + 38.6 + 2.0 + 112.2 - 92.8 + \Delta G_f + \Delta G_g$   
 $\Delta G_f + \Delta G_g = -48.6$  kcal.

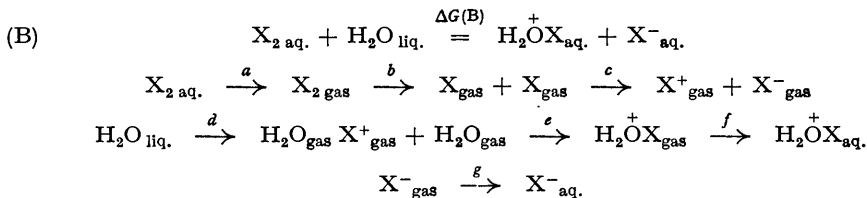
For chlorine,  $\Delta G = 4.5 = -1.0 + 50.4 + 2.0 + 112.2 - 105.1 + \Delta G_f + \Delta G_g$   
 $\Delta G_f + \Delta G_g = -54.0$  kcal.

The free energy of solution of  $\text{HOX}_{\text{gas}}$ ,  $\Delta G_g$ , can be estimated by comparison with the free energies of solution of the halogens  $\text{X}_{2\text{gas}}$  and the free energy of condensation of water  $\text{H}_2\text{O}_{\text{gas}}$ .  $\Delta G_g$  is considered to be  $-2 \pm 1$  kcal./mole for all three halogens.

Hence, we obtain the values for  $\Delta G_f$ , the free energies of formation of the oxygen-halogen bonds :



*Free Energies of Formation of  $\text{H}_2\text{O}^+\text{X}$  in Aqueous Solution.*—We can now turn to the calculation of the free energy of formation of the cation  $\text{H}_2\text{O}^+\text{X}$  in aqueous solution. The free energy of the reaction (B),  $\Delta G(\text{B})$ , is the sum of the free energies of steps  $a-g$  :



We must consider the free energies of steps  $e$  and  $f$ . For the free energies of step  $e$ , the calculated free energies for the reaction  $\text{X}_{\text{gas}} + \text{OH}_{\text{gas}} = \text{HOX}_{\text{gas}}$  are used.

The analogous reactions of the proton are as follows:  $\text{H}^+_{\text{gas}} + \text{H}_2\text{O}_{\text{gas}} \longrightarrow \text{H}_3\text{O}^+_{\text{gas}} \longrightarrow \text{H}_3\text{O}^+_{\text{aq.}}$ . The heat of solution of  $\text{H}^+_{\text{gas}}$  is 282 kcal. (Baughan, *J.*, 1940, 1403). If the heat of formation of  $\text{H}_3\text{O}^+_{\text{gas}}$  is equal to the heat of the reaction  $\text{H}_{\text{gas}} + \text{OH}_{\text{gas}} = \text{H}_2\text{O}_{\text{gas}}$  (120 kcal.), the heat of solution of  $\text{H}_3\text{O}^+_{\text{gas}}$  is 162 kcal. By analogy with  $\text{H}_3\text{O}^+$ , and from consideration of their size, the heats and free energies of solution of the ions  $\text{H}_2\text{O}^+\text{X}$  are estimated as follows (cf. Eley and Evans, *loc. cit.*) :

	$\text{H}_2\text{OI}^+$	$\text{H}_2\text{OBr}^+$	$\text{H}_2\text{OCl}^+$
$Q$ (heat evolved) .....	100	110	120
$\Delta G_f$ .....	-94	-103	-112

It is possible that the free energies  $\Delta G_e$  are underestimated. However, in that case the heats and free energies of solution of the ions  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}^+\text{X}$  are overestimated proportionally.

The free energy of reaction (B) is given by the relation  $\Delta G(\text{B}) = \Delta G_a + \Delta G_b + \dots + \Delta G_g$  :

For iodine,  $\Delta G(\text{B}) = 0.7 + 28.9 + (242.2 - 75.7) + 2.0 - 47 - 94 - 43 = 14$  kcal.

For bromine,  $\Delta G(\text{B}) = -0.2 + 38.6 + (274.6 - 82.1) + 2.0 - 47 - 103 - 53 = 30$  kcal.

For chlorine,  $\Delta G(\text{B}) = -1.0 + 50.4 + (300.3 - 87.3) + 2.0 - 52 - 112 - 58 = 42$  kcal.

The equilibrium constants  $K = [\text{H}_2\text{O}^+\text{X}][\text{X}^-]/[\text{X}_2]$  corresponding to the above free-energy changes at 25° are approximately  $10^{-10}$  for iodine,  $10^{-20}$  for bromine, and  $10^{-30}$  for chlorine.

The free energies  $\Delta G_e$  and  $\Delta G_f$  are admittedly somewhat uncertain, but the above values of the equilibrium constants are considered reliable to within a few powers of ten.

The conclusions that can definitely be drawn from the above calculations are as follows :

(1) The bare halogen cations  $\text{X}^+$  cannot exist in appreciable concentration in aqueous solution.

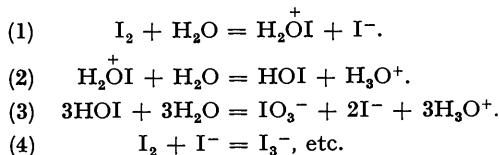
(2) The hydrated halogen cations  $\text{H}_2\text{O}^+\text{X}$  are much more stable. The iodine cation  $\text{H}_2\text{OI}^+$  is the only one, however, which appears to be sufficiently stable to allow preparation of a halogen solution in which an appreciable proportion of the halogen is present as a cation. Thus, if the iodide concentration in an iodine solution were lowered to  $10^{-12}\text{N}$ . by addition of a soluble silver salt, the calculated value for the equilibrium constant indicates that almost all the iodine in solution will be in the form of the cation  $\text{H}_2\text{OI}^+$  (provided no other reactions interfered; see below). On the other hand, in the case of bromine and chlorine, even at the lowest controllable halide concentrations, the calculations indicate that  $[\text{H}_2\text{O}^+\text{X}]/[\text{X}_2] \ll 1$ .

The experimental studies on the iodine cation presented in the following section confirm the theoretical predictions for this halogen, and lend strong support to the validity of the thermodynamic calculations for the other halogens.

#### *Section B. Experimental Studies on the Iodine Cation.*

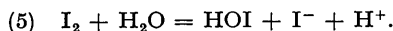
The calculations in the preceding section indicated that the stability of the hydrated iodine cation should permit an almost complete conversion of iodine into this cation at attainably low iodide concentrations. This conclusion has been confirmed by the experiments now to be described.

When iodine is dissolved in water, the ionisation (1) can be followed by a variety of reactions :



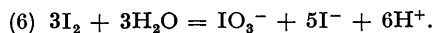
Formation of  $\text{H}_2\overset{+}{\text{O}}\text{I}$  is clearly favoured by a low iodide concentration. A low iodide concentration represses reactions of type (4); however, it facilitates the hydrolytic reactions (2, 3). The latter can be repressed by increasing the acid concentration; acid has no effect on the ionisation equilibrium (1). It is clear that the concentration of the iodine cation which can be produced is limited not only by its free energy of formation, but also by the free energies and velocities of the subsequent hydrolytic decompositions. For these latter reactions the following data are available.

Steps (1) and (2) in the above reaction scheme are generally represented by (5) :



The equilibrium constant of this hydrolysis reaction is  $3 \times 10^{-13}$  (Bray and Conolly, *loc. cit.*) and the reaction is very fast (Liebhafsky, *Z. physikal. Chem.*, 1931, **155**, A, 289).

The formation of iodate is generally represented by reaction (6) :



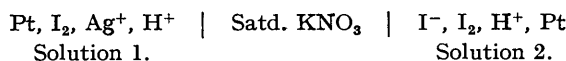
The equilibrium constant is  $4 \times 10^{-48}$  (Lundberg, Vestling, and Ahlberg, *J. Amer. Chem. Soc.*, 1937, **59**, 264). This reaction is very slow at appreciable iodide and acid concentrations. The rate of the iodate-iodide reaction at low iodide concentrations is given by the equation  $-\text{d}[\text{IO}_3^-]/\text{dt} = 2 \times 10^4[\text{IO}_3^-][\text{I}^-][\text{H}^+]^2$  moles  $\text{l}^{-1} \text{min}^{-1}$  (Abel, *Z. physikal. Chem.*, 1928, **136**, 186 *et seq.*). Combining this expression with the equilibrium data, we have for the initial rate of iodate formation

$$(7) \quad \text{d}[\text{IO}_3^-]/\text{dt} \simeq 8 \times 10^{-44} [\text{I}_2]^3/[\text{I}^-]^4[\text{H}^+]^4 \text{ moles } \text{l}^{-1} \text{min}^{-1}.$$

on the assumption that the system follows the same kinetics on both sides of the equilibrium.

The equilibrium constant of reaction (5) and the rate of reaction (6) determine the concentrations of iodine, iodide, and acid for which the hydrolytic decompositions of the iodine cation can be repressed.

*Preparation and Investigation of Solutions containing  $\text{H}_2\overset{+}{\text{O}}\text{I}$ .*—Solutions of iodine were prepared in which the iodide concentration was lowered by the addition of a soluble silver salt, and the removal of iodine (either by ionisation or by hydrolytic decomposition) was investigated by measuring the redox potentials of the solutions. Cells of the following type were employed.

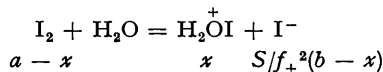


The acid concentrations and ionic strengths were always equal in solutions 1 and 2. The activity coefficients of the iodide ion in the two solutions can therefore be assumed equal, and the liquid-junction potential will be negligible. The E.M.F. of the experimental cell is then given by the expression

$$(8) \quad \text{E.M.F.} = (RT/2F) (\ln [\text{I}^-]_2^2/[\text{I}_2]_2 - \ln [\text{I}^-]_1^2/[\text{I}_2]_1)$$

where the subscripts refer to solutions 1 and 2.

If further hydrolytic changes are effectively repressed, ionisation is the only process by which molecular iodine is removed :



$a$  and  $b$  are the initial concentrations of iodine and silver, respectively, in solution 1,  $x$  is the concentration of the cation at equilibrium,  $S$  the solubility product of silver iodide, and  $f_{\pm}$  the mean ionic activity coefficient, where  $[\text{Ag}^+][\text{I}^-]f_{\pm}^2 = S$ . Inserting the appropriate values, we have for the E.M.F. in volts at  $25^\circ$  :

$$\text{E.M.F.} = 0.0296 (\log_{10} [\text{I}^-]_2^2/[\text{I}_2]_2 - \log_{10} [S^2/f_{\pm}^4(b - x)^2(a - x)])$$

and on rearrangement of the equation :

$$(9) \log_{10} (b-x)^2(a-x) = \frac{\text{E.M.F.}}{0.0296} - \log_{10} \frac{[\text{I}^-]_2^2}{[\text{I}_2]_2} + \log_{10} S^2 - \log_{10} f_{\pm}^4$$

If the activity coefficients are known, the above equation can be solved for the unknown  $x$ , and hence the thermodynamic ionisation constant  $K$  can be obtained :

$$(10) K = \frac{[\text{H}_2\text{OI}^+][\text{I}^-]f_{\pm}^2}{[\text{I}_2]} = \frac{x \left[ \frac{S}{f_{\pm}^2(b-x)} \right] f_{\pm}^2}{a-x} = \frac{xS}{(b-x)(a-x)}$$

#### EXPERIMENTAL.

The electromotive force cell was similar in design to that used by Everett and Wynne-Jones (*Proc. Roy. Soc.*, 1938, *A*, **169**, 190 *et seq.*). Platinum-gauze electrodes fitted into the two electrode compartments, which were connected with the salt bridge compartment by thin tubes ending in jets; the liquid junctions were formed in these jet tubes. The E.M.F. was measured with a Tinsley Vernier potentiometer. All measurements were made at  $25^\circ \pm 0.02^\circ$ . Conductivity water and reagents of analytical grade were used throughout. For each experiment two solutions were made. Solution 1 contained known concentrations of iodine, silver nitrate, and perchloric acid. Solution 2 contained known concentrations of perchloric acid, iodine, and iodide, allowance being made for the iodine-tri-iodide equilibrium (Jones and Kaplan, *J. Amer. Chem. Soc.*, 1928, **50**, 1845). The ionic strength was adjusted, when necessary, with sodium perchlorate. The solutions were made up, the cell filled and brought to constant temperature in a thermostat, and the E.M.F. measured 5 minutes after mixing. Readings of E.M.F. were then taken at intervals for some time. The iodine solution for solution 1 was always freshly made by shaking AnalaR iodine with water and filtering through a sintered-glass filter. The iodine-iodide stock solutions for solution 2 were prepared by weight. Standard thiosulphate was used as the halogen standard, and constant-boiling hydrochloric acid as the acid-base standard. The platinum electrodes were washed repeatedly with water and heated in an alcohol flame before use.

#### RESULTS.

Table I shows a set of typical experiments to determine the iodine ionisation constant. The initial iodine concentration and the iodide concentration are varied over nearly two powers of 10; the acid concentration range is 0.2—1.0N.

The activity coefficients are not known experimentally at these high concentrations. However, reasonable values can be calculated from the expression for the mean ionic activity coefficient (Davies, *J.*, 1938, 2093) :

$$(11) -\log_{10} f_{\pm} = 0.5I^{1/2}/(1 + I^{1/2}) - 0.2I$$

where  $I$  is the ionic strength of the solution. The solubility product of silver iodide is taken as  $1.0 \times 10^{-16}$  g.-ion/l. (Hass and Jellinek, *Z. physikal. Chem.*, 1932, **162**, 153). The last column in Table I gives the ionisation constants calculated as shown above from equations (9)—(11). The constants obtained are very good, especially in view of the nature of the solutions studied, in particular the uncertainties over activity coefficients, and the very low iodide concentrations in the presence of silver iodide.

The degree of constancy can be improved by employing a slightly different expression for the activity coefficients. In particular, in experiments such as the 4th and the 5th in the list, where both sodium perchlorate and perchloric acid are present in considerable concentrations, a lowering of the mean activity coefficient by the sodium salt improves the values for the ionisation constant. This decrease in  $f_{\pm}$  is not unexpected (Pearce and Nelson, *J. Amer. Chem. Soc.*, 1933, **55**, 3075; Scatchard, Prentiss, and Jones, *ibid.*, 1934, **56**, 805).

The most important conclusion from these experiments is, however, that, regardless of the expression used for the activity coefficients (even  $f_{\pm} = 1$  throughout), the ionisation constants show no trend with the concentration of any given species present in the solutions. If the removal of iodine were due to hydrolytic decomposition, the extent of this decomposition should of course be acid-dependent, so that an inverse variation of the apparent ionisation constant would be expected with acid concentration.

The thermodynamic ionisation constant of iodine is found to be  $1.2 \times 10^{-11}$ . This value is in good agreement with that predicted in the preceding section for the reaction  $\text{I}_2 + \text{H}_2\text{O} = \text{H}_2\text{OI}^+ + \text{I}^-$ . It is therefore certain that the cation under study is the hydrated cation or hypiodous acidium ion and not the base cation  $\text{I}^+$ .

TABLE I.

Ionisation. (Concentrations in g.-mols./litre.)

E.M.F. values are initial values which generally remain steady for several hours.

$10^6[I_2]$ , initial.	$10^3[Ag^+]$ , initial.	$\log_{10} \frac{[I^-]_2^2}{[I_2]_2}$	E.M.F. (volts).	$I$ .	$f_{\pm}$ .	$[H^+]$ .	$10^6[H_2OI^+]$ .	$10^{13}[I^-]$ .	$10^6[I_2]$ .	$10^{11}K$ .
1.77	7.95	0.035	0.524	1.0	0.89	1.0	1.60	19.8	1.74	1.4
3.00	15.6	0.035	0.542	1.0	0.89	0.9	2.82	9.83	1.90	1.2
23.6	5.00	0.035	0.500	1.0	0.89	0.75	4.75	510	188	1.1
23.6	10.0	0.035	0.511	1.0	0.89	0.60	9.60	285	140	1.5
23.6	5.00	0.035	0.485	1.0	0.89	0.40	4.86	914	187	1.9
					(0.79)					(1.2)
					(0.76)					(1.3)
7.15	8.77	-0.965	0.502	1.0	0.89	1.0	5.70	41.1	14.5	1.3
2.26	5.85	-0.965	0.495	1.0	0.89	1.0	1.80	31.2	4.57	1.0
2.26	5.85	-0.965	0.488	0.75	0.83	0.75	1.91	36.8	3.47	1.4
18.7	5.00	-0.965	0.470	0.50	0.78	0.50	4.64	448	141	0.9
7.15	9.75	-0.965	0.501	0.50	0.78	0.50	5.82	42.0	13.3	1.1
2.26	5.85	-0.965	0.490	0.50	0.78	0.50	1.75	40.0	5.13	0.8
5.40	10.0	-0.965	0.474	0.40	0.77	0.40	9.75	690	443	0.9
3.75	10.0	-0.965	0.498	0.30	0.76	0.30	3.36	26.1	3.89	1.3
6.78	5.85	-0.965	0.482	0.30	0.76	0.30	4.34	115	24.5	1.2
18.7	5.00	-0.965	0.457	0.20	0.77	0.20	5.00	712	137	1.5

The equilibrium constant for reaction (2) (p. 2737) is obtained by dividing the hydrolysis constant for reaction (b) by the ionisation constant (1):

$$K_2 = \frac{[HOI][H_3O^+]}{[H_2OI^+]} = \frac{[H_3O^+][I^-][HOI]f_{\pm}^2}{[I_2]} \bigg/ \frac{[H_2OI^+][I^-]f_{\pm}^2}{[I_2]} = 0.03$$

hence

$$(12) \quad [H_2OI^+] \simeq 35[H_3O^+][HOI]$$

In the experiments recorded in Table I there is present a small concentration of hypiodous acid, which decreases with increasing acid concentration. No correction for this equilibrium concentration of hypiodous acid has been applied to the values listed in Table I. It can be seen from equation (12) that this correction will lead to a decrease in the  $H_2OI^+$  concentration and in the ionisation constant ranging from approximately 3% when  $[H^+] = 1.0N$  to 12% when  $[H^+] = 0.2N$ .

TABLE II.

Iodate formation.

$10^6[I_2]$ , initial.	$10^3[Ag^+]$ , initial.	$\log_{10} \frac{[I^-]_2^2}{[I_2]_2}$	E.M.F.† (volts).	$[H^+]$ .	$f_{\pm}$ .	$10^6[HOI^+]$ .*	$10^{11}[I^-]$ .*	$[I_2]$ .*	$K$ .*
5.0	0.24	0.04	0.515	0.1	0.79	5.0	84	$1.6 \times 10^{-7}$	$1.6 \times 10^{-10}$
5.0	0.36	0.04	0.515	0.1	0.79	5.0	51	$6.0 \times 10^{-8}$	$2.7 \times 10^{-10}$
4.7	0.36	-0.50	0.472	0.01	0.89	4.7	41	$3.9 \times 10^{-9}$	$3.9 \times 10^{-9}$
26	50	-2.56	0.465	1.0	0.89	26	0.25	$1.1 \times 10^{-11}$	$4.7 \times 10^{-6}$
29	50	-1.57	0.463	0.27	0.76	29	0.35	$1.8 \times 10^{-12}$	$3.2 \times 10^{-7}$

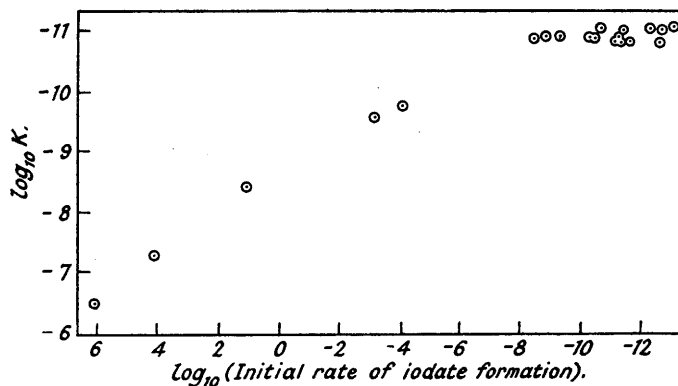
\* Apparent concentrations.

† Initial values.

Under the conditions of the experiments in Table I the rate of iodate formation given by equation (7) is negligible. When iodate equilibrium is attained after several days, considerable quantities of iodate have been formed, as is shown by the slow decrease of the E.M.F. with time from the steady value of the first few hours. In the experiments recorded in Table II, the iodide and/or acid concentrations have been deliberately lowered so as to accelerate the rate of iodate formation. It is observed that the apparent ionisation constants now vary with acid concentration in the manner expected for a hydrolytic reaction of this type.

In the figure, apparent ionisation constants are plotted against calculated rates of iodate formation. As long as the latter are small, the ionisation constants are fairly steady. When the rate of iodate formation becomes so fast that iodine is converted into iodate in a matter of hours or even more quickly, then a rapid fall in the apparent ionisation constants is observed. The fourth-power dependence of the rate of the iodate reaction on the iodide and acid concentrations places a sharp limit on the conditions under which solutions containing the cation  $H_2OI^+$  can be studied.

*Note on Previous Work.*—One previous attempt to determine the iodine ionisation constant merits special discussion (Murray, *J.*, 1925, **127**, 882). The method employed was to measure electrometrically the iodide concentration in an acid solution of iodine. The iodide concentration found was attributed entirely to ionisation, and the ionisation constant was taken to be equal to  $[I^-]^2 \cdot f_{\pm}^2 / I_2 = 1 \times 10^{-8}$  ( $[I_2] = [I_2]$  initial). This method depends on (a) ionisation having a much greater tendency to occur than hydrolysis, and (b) the absence of iodide impurities.



Condition (a) is not adequately fulfilled except at high acid concentrations, as shown by the present work; nor does it appear that condition (b) is satisfied. It is unlikely that iodide impurities can have been eliminated in the previous work, as shown by some new experiments illustrated in Table III. The iodide concentrations in various acid solutions of iodine were

TABLE III.

Sample.*	$[H^+]$ .	$10^6[I_2]$ .	$10^6[I^-]$ .	$100[I^-]/[I_2]$ .	$10^8[I^-]^2 f_{\pm}^2 / [I_2]$ .
1	0.10	17.5	5.76	3.29	18.4
2	0.10	54.5	4.00	0.73	2.0
3	0.10	26.5	3.63	1.37	3.2
4	0.10	3.60	1.76	4.88	5.4
4	0.10	3.60	1.74	4.84	5.4
5	0.10	47.0	2.92	0.62	1.2
6	0.25	20.2	2.45	1.22	1.6

\* 1. Iodine. 2, 3, 4. "AnalaR" Iodine. 5, 6. "AnalaR" Iodine freshly resublimed.

measured electrometrically. The apparatus, especially the electrodes, was washed repeatedly with conductivity water before use. The results show that the iodide concentration and the apparent ionisation constant depend on the sample of iodine used. The iodide concentration decreases with repeated purification of the iodine. It is concluded that this method is inapplicable to the study of the ionisation of iodine. The method developed in the present work is, of course, unaffected by small iodide impurities.

*Conclusions.*—It has been shown that the thermodynamic stability of the iodine cation in aqueous solution is governed essentially by the equilibrium constants of reactions (1), (2), and (3). The equilibrium constants of reactions (1) and (2) are found to be  $1 \times 10^{-11}$  and  $3 \times 10^{-2}$ , respectively. For practical purposes the third equilibrium condition (3) may be replaced by the condition that the rate of iodate formation must be sufficiently slow. This analysis of the factors governing the stability of the iodine cation should be of direct practical application in many iodination reactions, in which the iodine cation can be the active iodinating agent.

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